DOI: 10.1080/00986445.2012.759563

Cationic Dye Removal from Aqueous Solutions Using Ionic Liquid and Nonionic Surfactant-Ionic Liquid Systems: A Comparative Study Based upon Experimental Design

Z. TALBI,[1] B. HADDOU,[1] H. GHOUAS,[1]
M. KAMECHE,[1] Z. DERRICHE,[1] AND C. GOURDON[2]

[1]Faculté des Sciences, Département de Chimie, Laboratoire de Physico-Chimie des Matériaux, U. S. T. Oran, Oran, Algeria
[2]Laboratoire de Génie Chimique, UMR, BP, Toulouse, France

In order to separate methylene blue from aqueous solution, a novel method based upon liquid-liquid extraction, using a nonionic surfactant-ionic liquid system as extracting phase, was investigated. A comparative study was carried out with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, known as [C4mim]PF6. By using the nonionic surfactant-ionic liquid system, the extraction efficiency could reach 97.8%, indicating that the addition of nonionic surfactant (Triton X-114) significantly improves the extraction of methylene blue. Under optimal conditions, the dye concentration in the effluent showed an almost 50-fold reduction. However, the extraction extent of methylene blue was found to be low at low pH values, and in the presence of K_2CO_3, which may be useful for surfactant-ionic liquid system regeneration.

Keywords Cloud point extraction; Ionic liquid; Methylene blue; Nonionic surfactant

Introduction

For two decades, ionic liquids (IL) have been essential in various fields, in particular electrochemistry (electrolytic deposition of metals and electrolyte batteries), process engineering (thermal fluids), synthesis (solvent extraction, separation, and catalysis), and as solvents (organic reactions). Originally developed for their electrochemical properties, they were used as reaction solvents from the 1980s on and the interest in this type of compound is rapidly increasing.

An ionic liquid is a salt in the liquid state. In some cases, the term has been restricted to salts whose melting points are below 100°C. Their appealing features include a practically negligible vapor pressure under typical conditions of temperature and high electrical conductance (Olivier-Bourbigou et al., 2010). Moreover, the high density of imidazolium-based ILs relative to water makes them excellent extractants. In fact, the typical density difference between ionic liquids and common organic solvents as well as water favors rapid settling in phase-separation devices

Address correspondence to B. Haddou, Faculté des Sciences, Département de Chimie, Laboratoire de Physico-Chimie des Matériaux, U. S. T. Oran, BP 1505, M'Nouar, Oran, 31000 Algeria. E-mail: Boumediene74@yahoo.fr

used in separation processes (Poole and Poole, 2010). On the other hand, their miscibility with water can be complete (hydrophilic IL) or partial (hydrophobic IL). This behavior is mainly due to the nature of the anion (Shvedene et al., 2005), which forms hydrogen bonds, for instance, in the case of 1-butyl-3-methylimidazolium chloride [C4mim]Cl. The biphasic system is, therefore, formed by combining water/[C4mim]Cl and inorganic salt above a certain critical concentration (Safavi et al., 2008). He et al. (2005) used [C4mim]Cl to separate testosterone and epitestosterone from an aqueous solution. Other works based on ionic liquids and water-structuring salts have been reported (e.g., protein extraction with a series of ionic liquids, by Pei et al. (2009)). Vijayaraghavan et al. (2006) used *N*-butyl, *N*-methyl pyrrolidinium bis (trifluoromethanesulfonyl) amide to extract azo dye from water. The initial extraction efficiency was about 50%, while, with two or three extraction stages, it easily reached 95%. Li et al. (2007) investigated acid dye extractions from aqueous solutions using 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim]PF6); the ion exchange process was predominant for extraction of dyes and obviously responsible for the high distribution constant.

Hence, the aim of this work was to use a mixed micelle system made of a small amount of IL ([C4mim]PF6) (from 0.1 to 1.3 wt.%) with an appropriate concentration (from 2 to 6 wt.%) of nonionic surfactant (TX-114) for the separation of a hydrophilic dye (methylene blue) often used in the textile industry. First, the dye separation was achieved using ionic liquid ([C4mim]PF6). Then we carried out a comparative study with cloud point extraction using a nonionic surfactant-ionic liquid system (TX-114/[C4mim]PF_6). This method includes simultaneous cloud point and solubilization phenomena in a nonionic surfactant medium.

Most polyethoxylated nonionic surfactants in aqueous solutions form two phases above the cloud point (T_c): a surfactant-rich phase (coacervate) and a dilute phase, in which the concentration of the surfactant is close to its critical micelle concentration (CMC) (Fischer and Matthias, 2011; Haddou et al., 2003, 2006; Li et al., 2009). Therefore, the solute initially present in the solution and bound to the micelles may be favorably extracted into the surfactant-rich phase after increasing the temperature above T_c. Many compounds have been extracted using cloud point extraction: metal ions (Citak and Tuzen, 2010; Silva et al., 2009; Sun and Wu, 2011; Xiang et al., 2011), organic compounds (Ghouas et al., 2012; Haddou et al. 2003, 2006, 2011; Li and Chen, 2008; Taechangam et al., 2009; Talbi et al. 2009; Wang et al., 2007, and proteins (Malzert-Fréon et al., 2008).

Materials and Methods

Reagents

The ionic liquid used in this work was commercial 1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim]PF6), obtained from Solvionic (Toulouse, France). Triton X-114 (octyl phenol polyethylene glycol ether) was supplied by Sigma-Aldrich. The critical micelle concentration of TX-114 is 1.7×10^{-4} M. The cloud point of TX-114 at 1 wt.% in water was obtained at 24°C. Methylene blue (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride), $C_{16}H_{18}ClN_3S$, having a molecular weight 319.85 g/mol, a solubility in water of 40 g/L, and maximum absorption wavelength of 460 nm, was supplied by Acros. Potassium carbonate (K_2CO_3) was purchased from Fluka. The pH values of the solutions were adjusted between 2 and 12 by adding hydrochloric acid and sodium hydroxide as appropriate.

Apparatus

The determination of the cloud point was achieved using a Mettler FP 900 apparatus: the temperature of the sample, placed in a cell, was measured using a precise sensor placed in a small oven. At the bottom of the measuring cell, a luminous source and an optic driver illuminated the sample. The crossed sample light was converted by a photoelectric cell into an electric signal proportional to the transmitted light intensity. The transmission of light was measured continuously, when the cell temperature increased linearly according to the chosen heating rate. The cloud point may be defined as the temperature at which the unique limpid phase becomes cloudy, inducing a transmission decrease. The dye concentration was determined using a spectrophotometer (SAFAS type MC2).

The extraction efficiency of methylene blue can be calculated by using

$$E = (C_i V_i - C_d V_d)/C_i V_i \tag{1}$$

where C_i is initial concentration of methylene blue, C_d is concentration of methylene blue in dilute phase, V_i is initial volume of solution (10 mL), and V_d is volume of dilute phase.

Procedure

A typical cloud point experiment required the following steps: 10 mL of solution containing methylene blue (7 mg/L) was prepared in distilled water, the IL at 0.1, 0.4, 0.7, 1, and 1.3 wt.% (for the extraction using surfactant-ionic liquid system, Triton X-114 was added at 2, 3, 4, 5, and 6 wt.%, respectively). The mixture was poured into graduated cylinders and heated in a precise thermostated water bath for 2 h to reach phase separation (dilute and concentrated phases). The volumes of both phases were registered. A small amount of the dilute phase was removed with a syringe and analyzed with a spectrophotometer to determine the dye concentration.

Results and Discussion

Binary and Pseudo-Binary Phase Diagrams

Aqueous solutions of polyethoxylated nonionic surfactants are sensitive to temperature because their hydrophilic groups undergo gradual desolvation during heating (Haddou et al., 2003). Above a certain temperature called cloud point (T_c), the surfactant becomes less soluble in water and concentrated in another phase (coacervate). The binary and pseudo-binary phase diagrams of water/TritonX-114 and water/Triton X-114/[C4mim]PF6 systems are shown in Figure 1. The ionic liquid increases the cloud point of Triton X-114 ($T_c = 21°C$ at 1 wt.% of TX-114) significantly due to the existence of important interactions between surfactant and IL (Haddou et al., 2006). Furthermore, the incorporation of ionic liquid into the nonionic micelles causes electrostatic repulsion between the micelles, thus hindering the coacervate phase formation and raising the cloud point.

The effect of the amount of salts on the phase diagram of pseudo-binary systems was investigated. It can be easily shown that the addition of K_2CO_3 lowers the cloud point of the Triton X-114/1.4 wt.% [C4mim]PF6 system significantly. This phenomenon is due to the salting out of the surfactant, induced by the solvated electrolyte

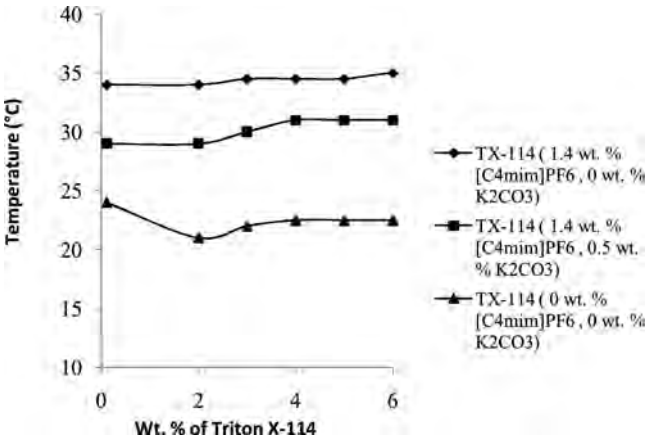

Figure 1. Effect of the salt on the cloud point temperature of Triton X-114.

(Miyagishi et al., 2001). In fact, Figure 1 shows that 0.5 wt.% of K_2CO_3 is largely sufficient to lower the cloud point of 2 wt.% Triton X-114/1.4 wt.%[C4mim]PF6 system from 35°C down to 29°C. Indeed, the presence of K_2CO_3 in water (solubility 1120 g/L at 25°C) makes the surfactant more hydrophobic.

Extraction of Methylene Blue Using Ionic Liquid [C4mim]PF6

The extraction results of methylene blue from its aqueous solutions at 7 mg/L by the ionic liquid (used alone) may be presented by two variables: wt.% ionic liquid (X_{IL}) and temperature (T), whose responses are: percentage of extracted solute (E) and residual concentration of solute ($X_{s,w}$) in the dilute phase. For each parameter determined by considering central composite designs (Box and Draper, 1987), the results were analyzed by an empirical fitting. In this mathematical analysis, the experimental data allowed the determination of the polynomial model constants, which were adjusted. The models were checked by plotting computed data against experimental results. The quadratic correlation was chosen so as to yield a slope along with a regression coefficient (R^2) close to unity.

The quadratic equations for the two properties (E, $X_{s,w(IL)}$), whose reliabilities were checked beforehand, may be presented as follows:

$$E_{(IL)} = 41.099 + 44.277X_{IL} + 2.105\,T + 1.533X_{IL}T - 48.805X_{IL}^2 - 0.0569\;T^2 \quad (2)$$

$$X_{s,w_{(IL)}} = 4.0292 - 3.2120X_{IL} - 0.1405\,T - 0.103X_{IL}T + 3.381\;X_{IL}^2 + 0.0038\,T^2 \quad (3)$$

Figure 2 represents the three-dimensional iso-response curves of the studied properties fitted to the quadratic model (Equations (2) and (3)). $X_{s,w(IL)}$ increases with temperature, together with a decrease of E. For example, at $X_{IL=}$ 0.1 wt.%, E decreases from 65.12 to 17.01 when the temperature increases from 25° to 50°C (Table I). The solubility of methylene blue in water increases from 25° to 50°C (Haddou et al., 2007). Indeed, the dye becomes more hydrophilic at higher temperature; the hydrophilic character of methylene blue is due primarily to its molecular structure, in particular to nitrogen and sulfur atoms that could interact with water

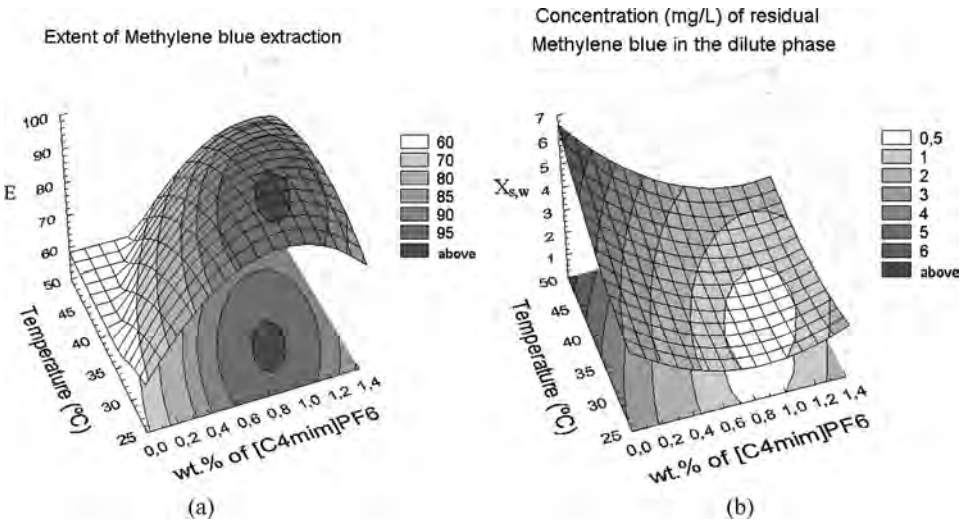

Figure 2. Three-dimensional iso-response curves smoothed by a quadratic model (Equations (2) and (3)): (a) $E_{(IL)} = f(X_{IL}, T)$, (b) $X_{(IL)} = f(X_{IL}, T)$.

molecules through hydrogen bonding. Furthermore, this character may be enhanced when temperature rises (Guilherme et al., 2003). Pei et al. (2012) proved that [PF6] anion is one of the major components of the [C4mim]PF6/methylene blue associate. Indeed, the associate was formed by cation of the cationic dye and anion of the ionic liquid. They proved also that the molar ratio between the dye-cation and [PF6] anion in the associate was close to 1:1. The spontaneity of the association formation process was confirmed by Gibbs free energy changes accompanying these processes. Furthermore, the associate formation is exothermic. Hence, the tendency to form [C4mim]PF6/methylene associates was found to decrease with increasing temperature.

One can notice in Figure 2(b) that the increase of X_{IL} favors methylene blue extraction. In fact, for 1.3 wt% of IL, the concentration of dye in the dilute phase decreases to 1.38 mg/L at 50°C, corresponding to an increase of E to 80.02% (Table I). The nature of the dye-ionic liquid interaction has received a great deal

Table I. Pure [C4mim]PF6: Some experimental results of the extraction parameters $E_{(IL)}$, $X_{s,w(IL)}$, R^2, and $X_{s,0}/X_{s,w}$

[T (°C), X_{IL} (wt.%)]	E (%)	$X_{s,w(IL)}$ (mg/L)	$X_{s,0}/X_{s,w}$ [a]
[25, 0.1]	65.12	2.44	2.86
[35, 0.1]	53.14	3.28	2.13
[50, 0.1]	17.01	5.80	1.20
[25, 0.7]	91.50	0.59	11.86
[35, 0.7]	88.12	0.83	8.43
[50, 0.7]	63.99	2.52	2.77
[50, 1.3]	80.02	1.38	5.07

[a] $X_{s,0} = 7$ mg/L (initial concentration of methylene blue).

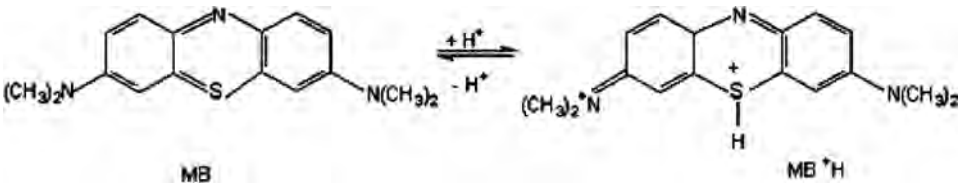

Figure 3. Structure of methylene blue in acidic and basic media.

of attention from researchers (Iglesia and Montenegro, 1996). The existence of effective ion association between IL and dye with opposite charge allows an IL with a large cationic site to form ion pairs with negatively charged sulfonate groups of dyes (Buwalda et al., 1999). These complexes aggregate and precipitate readily in the solution at room temperature. But when the latter increases, the aggregates dissociate and the dye returns to solution (Safavi et al., 2008). However, methylene blue is a cationic dye (Figure 3). So, it seems reasonable that the IL anionic site (hexafluorophosphate) associates with the 3,7-bis(dimethylamino)-phenothiazin-5-ium cation to form the [C4mim]PF6-methylene blue 1:1 complex (Pei et al., 2012). In addition, it was also found that [C4mim]PF6 forms quite strong associates with methylene blue (Figure 3), giving an association constant as high as 10^6 $(L/mol)^2$.

Extraction of Methylene Blue with Triton X-114/[C4mim]PF_6 System

When the surfactant-ionic liquid system was used for the extraction of methylene blue from its aqueous solutions (7 mg/L), temperature was maintained constant at 35°C (the minimum temperature necessary for phase separation in the Triton X-114/[C4mim]PF_6 system; Figure 1). Extraction results are given according to two variables: wt.% of ionic liquid (X_{IL}), and wt.% of Triton X-114 (X_T). The responses studied were: percentage of extracted solute (E), residual concentrations of solute ($X_{s,w}$) in the dilute phase, and coacervate volume fraction at equilibrium (ϕ_C)

As mentioned previously, the quadratic correlation for E, $X_{s,w}$, and φ_C was chosen to give a slope and a regression coefficient (R^2) close to unity.

$$E_{(IL/TX-114)} = 58.291 + 2.829X_T + 43.264X_{IL} - 4.388X_TX_{IL} + 0.472X_T^2 - 12.797X_{IL}^2 \quad (4)$$

$$X_{s,w_{(IL/TX-114)}} = 2.923 - 0.198X_T - 3.0355X_{IL} + 0.3075X_TX_{IL} - 0.033X_T^2 + 0.898X_{IL}^2 \quad (5)$$

$$\phi_{C(IL/TX-114)} = -0.462 + 0.0658X_T + 1.666X_{IL} - 0.0083X_TX_{IL} + 0.005X_T^2 - 0.0416X_{IL}^2 \quad (6)$$

Figure 4 represents the three-dimensional iso-response curves of the studied properties fitted to the quadratic model (Equations (4)–(6)). One can notice in Figure 4 that the combination of Triton X-114 with [C4mim]PF6 improves the extraction efficiency of methylene blue significantly (Figures 2 and 4). For instance, E reaches 66.03% using the system 1 wt.% Triton X-114/0.1 wt.% [C4mim]PF6 (Table II) instead of 53.14% using 0.2 wt.% of [C4mim]PF6 (Table I) at 35°C

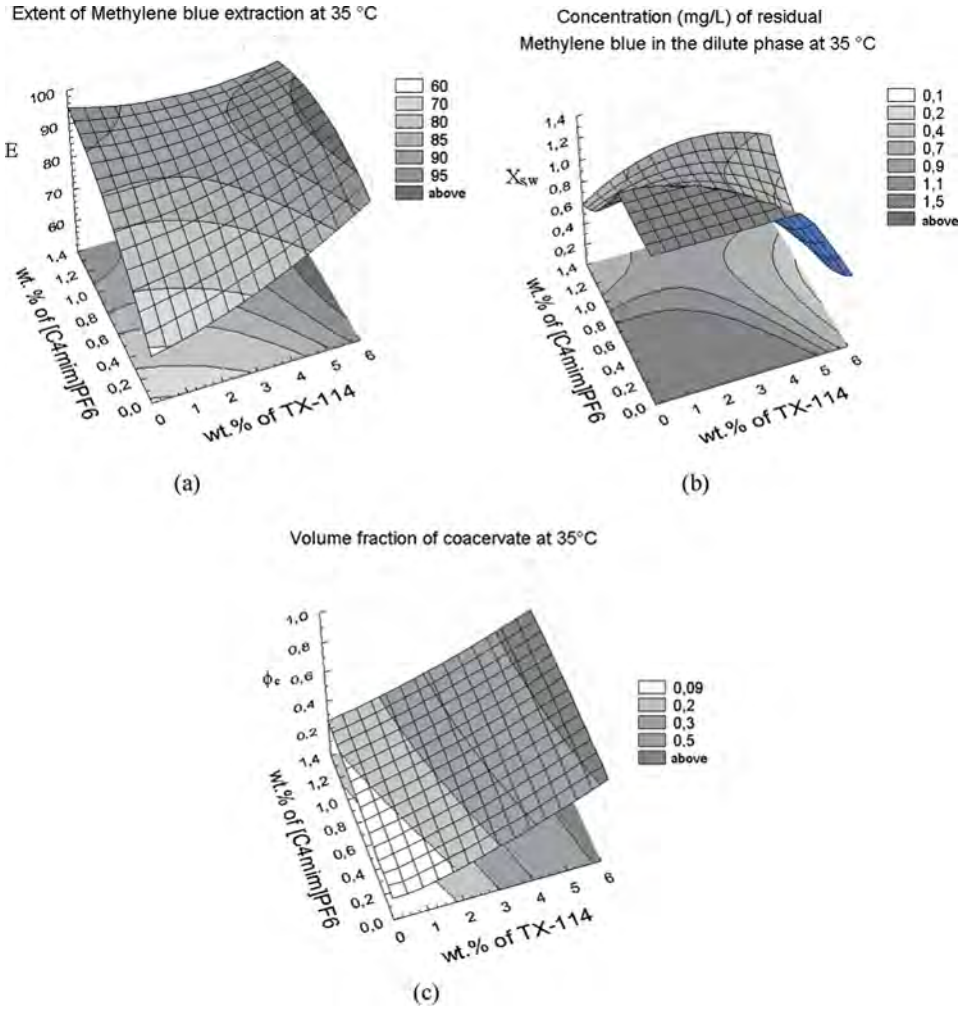

Figure 4. Three-dimensional iso-response curves smoothed by a quadratic model (Equations (4)–(6)): (a) $E_{(IL/TX\text{-}114)} = f(X_T, X_{IL})$, (b) $X_{(IL/TX\text{-}114)} = f(X_T, X_{IL})$, (c) $\phi_{C(IL/TX\text{-}114)} = f(X_T, X_{IL})$. (Figure provided in color online.)

(Figures 2(a) and 4(a)). These results are supported by the partition coefficient ($K = C_d/C_c$; C_d is concentration of solute in the dilute phase; C_c is concentration of solute in coacervate) of methylene blue relative to water at 35°C (Tables III and IV). K decreases when X_T and X_{IL} increase. This can be explained by the micellar solubilization effect of nonionic surfactant. Thus, higher amounts of the neutral ionic liquid-dye 1:1 complex are incorporated into the nonionic micelles and concentrate in the coacervate (Safavi et al., 2008). In contrast, our previous work relative to the extraction of methylene blue by 2 wt.% of pure Triton X-114 (at 35°C) (Haddou et al., 2007) gave an efficiency that never exceeded 50%.

In Figure 4(b), it is shown that the residual dye concentration, Xs,w, versus X_T and X_{IL} goes through a minimum. Hence, at optimal concentrations of IL and

Table II. [C4mim]PF6/TX-114 system: Some experimental results of the extraction parameters $E_{(IL/TX\text{-}114)}$, $X_{s,w(IL/TX\text{-}114)}$, ϕ_C, and $X_{s,0}/X_{s,w}$

[X_{IL} (wt.%), X_T (wt.%)]	$E_{(IL,TX\text{-}114)}$ (%)	$X_{s,w(IL,TX\text{-}114)}$ (mg/L)	ϕ_C	$X_{s,0}/X^a_{s,w}$
[0.1, 1]	66.03	2.37	0.05	2.95
[0.7, 1]	81.83	1.27	0.12	5.51
[1.4, 1]	90.04	0.69	0.15	10.14
[0.1, 6]	92.94	0.49	0.55	14.28
[0.7, 6]	97.80	0.15	0.60	46.66
[1.4, 6]	90.53	0.66	0.65	10.60

Table III. Partitioning of methylene blue at 1.3 wt.% [C4mim]PF6 and different concentrations of Triton X-114 (35°C)

$C_{TritonX114}$ (wt.%)	2	3	4	5	6
K	0.109	0.142	0.110	0.088	0.073

Table IV. Partitioning of methylene blue at 2 wt.% of Triton X-114 and different concentrations of [C4mim]PF6 (35°C)

$C_{[Bmim]PF6}$ (wt.%)	0.1	0.4	0.7	1	1.3
K	0.308	0.213	0.162	0.100	0.109

Triton X-114 ($X_{IL} = 0.7$ wt.%; $X_T = 6$ wt.%), the dye concentration in the effluent can be reduced to 0.15 mg/L (an almost 50-fold reduction), whereas, in our previous work (Haddou et al., 2007), Xs,w could not show more than a 7-fold reduction (1 mg/L) with 6 wt.% Triton X-114 (at 35°C).

In order to increase the concentration factor of a solute, a minimal volume fraction of coacervate (ϕ_C) should be obtained. Hence, according to Figure 4(c), ϕ_C is low at low surfactant concentration (X_T). But surfactant concentration reduction is not favorable to high extraction (Figure 4(a)), while high surfactant concentrations increases ϕ_C (Figure 4(c)). So the optimization of the process requires a compromise between the three studied parameters E, $X_{s,w}$, and ϕ_C.

Effect of pH on Extraction Efficiency of Methylene Blue

Extraction efficiency of methylene blue was studied as a function of pH. The results obtained using Triton X-114/[C4C1im]PF_6 system and [C4mim]PF6 alone are shown in Figure 5. As can be seen in Figure 5, the maximal extraction efficiency is observed at basic pH, where the neutral form (BM) of methylene blue molecule is predominant (Figure 3). Upon a decrease in pH, the recovery of methylene blue

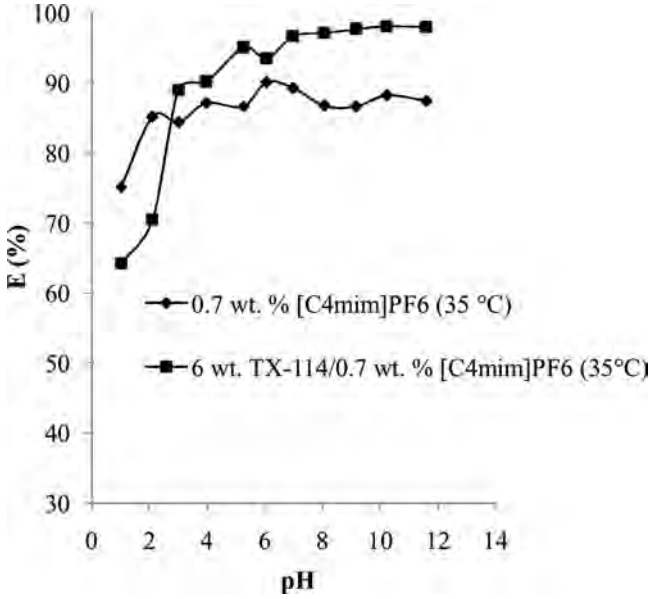

Figure 5. Effect of pH on extraction efficiency (*E*).

into Triton X-114/[C4mim]PF_6 system decreases, and at pH nearly equal to 1, the extraction efficiency of methylene blue becomes important (60%). The pK_a value of methylene blue is about 8.2. At lower pH, the studied dye is protonated (BM^+H), and its ionic characteristics increase, leading to less solubilization in the hydrophobic micelles of nonionic surfactant. In contrast, at basic pH the dye is easily solubilized into micelles. Under this condition, the neutral form of methylene blue (Figure 3) behaves as a hydrophobic molecule. The same behavior is observed in the absence of Triton X114. At acidic pH, the dye is charged positively, and the interactions between the charged groups of methylene blue and the imidazolium moiety of the IL are repulsive, leading to a weaker complexation and to dye precipitation.

Effect of Salt on Extraction

The effect of salt was also investigated. One can notice in Figure 6 that the addition of K_2CO_3 (between 0 and 3.5 wt.%) to the mixture containing 7 mg/L of methylene blue, 0.7 wt.% [C4mim] PF_6, and 6 wt.% Triton X114 decreases the extraction efficiency (*E*) of the dye (from 97.5% to 20.15%) considerably. In the absence of surfactant, (*E*) of methylene blue decreases from 89.5% to 41.12% (Figure 6). This finding is consistent with a previous work using testosterone (He et al., 2005). The high affinity of inorganic salt for water molecules induces dehydration of ionic liquid, which affects methylene blue/[C4mim]PF6 complex stability. Potassium carbonate (K_2CO_3) is known for its ability to form aqueous two-phase systems with some ionic liquids (Adebowole and Adebowole, 2007; Pei et al., 2009). For example, a biphasic system may be formed by combining water/[C_4mim]Cl and K_2CO_3 above a certain

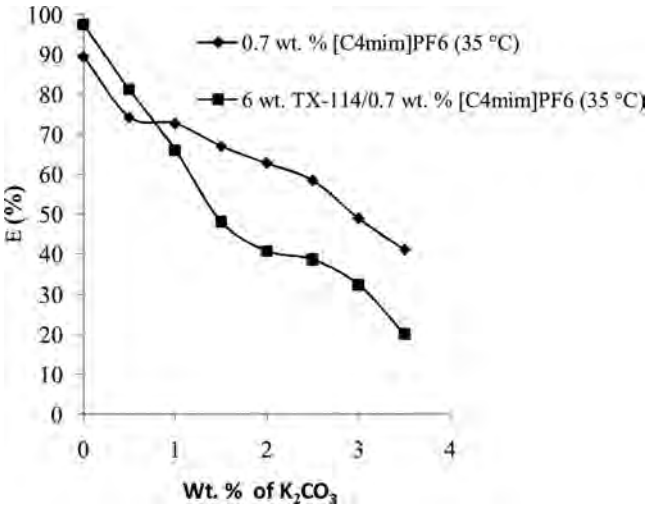

Figure 6. Effect of K_2CO_3 on the extraction efficiency (*E*) of methylene blue using Triton X-114/[C4mim]PF6 system and pure [C4mim]PF6.

critical concentration. This salt (K_2CO_3) decreases the extraction efficiency of steroids in the system [C4mim]Cl/K_2CO_3 (He et al., 2005).

Conclusions

A liquid-liquid extraction process using an imidazolium-based ionic liquid, [C4mim]PF6, was employed to separate methylene blue from its aqueous solutions. The extraction results were satisfactory and confirm that ionic liquids are potential solvents for the extraction of methylene blue as well as the conventional processes. It is found that the combination of [C4mim]PF6 and Triton X-114 in a cloud point extraction process improves the extraction qualitatively and quantitatively. The hydrophobic interactions between the dye and IL and/or nonionic surfactant were obviously the driving force of this extraction. In addition, the acidic pH and the presence of K_2CO_3 induce a significant decrease in extraction. They can also be exploited for the back-extraction of cationic dye and consequent regeneration of the coacervate phase of nonionic surfactant.

References

Adebowole, Y. A., and Adebowole, K. O. (2007). The influence of kosmotropic and chaotropic salts on the functional properties of *Mucuna pruriens* protein isolate, *Int. J. Biol. Macromol.*, **40**(2), 119–125.

Box, G., and Draper, N. (1987). *Empirical Model Building and Response Surfaces*, John Wiley & Sons, New York.

Buwalda, R. T., Jonker, J. M., and Engberts, J. B. F. N. (1999). Aggregation of azodyes with cationic amphiphiles at low concentrations in aqueous solution, *Langmuir*, **15**, 1083–1089.

Citak, D., and Tuzen, M. (2010). A novel preconcentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry, *J. Food Chem. Toxicol.*, **5**, 1399–1404.

Fischer, I., and Matthias, F. (2011). Direct determination of the composition of aqueous micellar two-phase systems (AMTPS) using potentiometric titration—A rapid tool for detergent-based bioseparation, *Colloids Surf. A: Physicochem. Eng. Aspects*, **337**, 93–102.

Ghouas, H., Haddou, B., Kameche, M., Derriche, Z., and Gourdon, C. (2012). Extraction of humic acid by coacervate: Investigation of direct and back processes, *J. Hazard Mater.*, **205–206**, 171–178.

Guilherme, M. R., Silva, R., Girotto, E. M., Rubira, A. F., and Muniz, E. C. (2003). Hydrogels based on PAAm network with PNIPAAm included: Hydrophilic–hydrophobic transition measured by the partition of Orange II and Methylene Blue in water, *J. Polym.*, **44**, 4213–4219.

Haddou, B., Canselier, J. P., and Gourdon, C. (2003). Purification of effluents by two-aqueous phase extraction, *Chem. Eng. Res. Des.*, **81**, 1185–1192.

Haddou, B., Canselier, J. P., and Gourdon, C. (2006). Cloud point extraction of phenol and benzyl alcohol from aqueous stream, *Sep. Purif. Technol.*, **50**, 114–121.

Haddou, B., Bouberka, Z., Taibi, A., Bouabdesselam, H., and Derriche, Z. (2007). Separation of neutral red and methylene blue from waste water using two-aqueous phase extraction, *Sep. Sci. Technol.*, **42**(12), 2677–2691.

Haddou, B., Guitri, N., Debbab, A., Gourdon, C., and Derriche, Z. (2011). Cloud point extraction of Orange II and Orange G using neutral and mixed micelles: Comparative approach using experimental design, *Sep. Sci. Technol.*, **46**(5), 734–743.

He, C., Li, S., Liu, H., Li, K., and Liu, F. (2005). Extraction of testosterone and epitestosterone in human urine using aqueous two-phase systems of ionic liquid and salt, *J. Chromatogr. A*, **1082**, 143–149.

Iglesia, E., and Montenegro, L. (1996). Determination of critical micelle concentration of some surfactants by three techniques, *J. Phys. Chem.*, **100**, 1227–1234.

Li, J. L., and Chen, B.-H. (2008). Recovering phenanthrene from spiked sand by a combined remediation process of micellar solubilization and cloud-point extraction, *J. Chin. Inst. Chem. Eng.*, **39**(4), 337–342.

Li, C., Xin, B., Xu, W., and Zhang, Q. (2007). Study on the extraction of dyes into a room-temperature ionic liquid and their mechanisms, *J. Chem. Technol. Biotechnol.*, **82**, 1996–2004.

Malzert-Fréon, A., Benoît, J.-P., and Boury, F. (2008). Interactions between poly(ethylene glycol) and protein in dichloromethane/water emulsions: A study of interfacial properties, *Eur. J. Pharm. Biopharm.*, **69**, 835–843.

Miyagishi, S., Okada, K., and Asakawa, T. (2001). Salt effect on critical micelle concentrations of nonionic surfactants, N-acyl-N-methylglucamides (MEGA-n), *J. Colloid Interface Sci.*, **238**, 91–95.

Olivier-Bourbigou, H., Magna, L., and Morvan, D. (2010). Ionic liquids and catalysis: Recent progress from knowledge to applications, *Appl. Catal. A: Gen.*, **373**, 1–56.

Pei, Y., Wang, J., Wu, K., Xuan, X., and Lu, X. (2009). Ionic liquid-based aqueous two-phase extraction of selected proteins, *Sep. Purif. Technol.*, **64**, 288–295.

Pei, Y., Liu, J., Yan, Z., Li, Z., Fan, J., and Wang, J. (2012). Association of ionic liquids with cationic dyes in aqueous solution: A thermodynamic study, *J. Chem. Thermodyn.*, **47**, 223–227.

Poole, C. F., and Poole, S. K. (2010). Extraction of organic compounds with room temperature ionic liquids, *J. Chromatogr. A*, **1217**, 2268–2286.

Safavi, A., Abdollahi, H., Maleki, N., and Zeinali, S. (2008). Interaction of anionic dyes and cationic surfactants with ionic liquid character, *J. Colloid Interface Sci.*, **322**, 274–280.

Shvedene, N. V., Borovskaya, S. V., Svirodov, V. V., Ismailova, E. R., and Pletnev, I. V. (2005). Measuring the solubilities of ionic liquids in water using ion-selective electrodes, *Anal. Bioanal. Chem.*, **381**, 427–430.

Silva, E. L., Roldan, P. dos S., and Giné, M. F. (2009). Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water samples by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optic emission spectrometry, *J. Hazard. Mater.*, **171**, 1133–1138.

Sun, M., and Wu, Q. (2011). Cloud point extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr (III) in human serum samples, *J. Pharm. Biomed. Anal.*, **60**, 14–18.

Taechangam, P., Scamehorn, J. F., Osuwan, S., and Rirksomboon, T. (2009). Effect of nonionic surfactant molecular structure on cloud point extraction of phenol from wastewater, *J. Colloids Surf. A: Physicochem. Eng. Aspects*, **347**, 200–209.

Talbi, Z., Haddou, B., Bouberka, Z., and Derriche, Z. (2009). Simultaneous elimination of dissolved and dispersed pollutants from cutting oil wastes using two aqueous phase extraction methods, *J. Hazard. Mater.*, **163**(2–3), 748–755.

Vijayaraghavan, R., Vedaraman, N., Surianarayanan, M., and MacFarlane, D. R. (2006). Extraction and recovery of azo dyes into an ionic liquid, *Talanta*, **69**, 1059–1062.

Wang, L., Jiang, G.-B., Cai, Y.-Q., He, B., Wang, Y.-W., and Shen, D.-Z. (2007). Cloud point extraction coupled with HPLC-UV for the determination of phthalate esters in environmental water samples, *J. Environ. Sci.*, **19**, 874–878.

Xiang, G., Wen, S., Wu, X., Jiang, X., He, L., and Liu, Y. (2011). Selective cloud point extraction for the determination of cadmium in food samples by flame atomic absorption spectrometry, *Food Chem.*, **132**(1), 532–536.